11.11 QUALITY CONTROL (WATER SAMPLING)

11.11.1 Filter Blanks

A. EQUIPMENT

1. One 500ml wide-mouth polyethylene collection bottle (Nalgene or equivalent)

2. One Swin-Lok filter holder (with 47mm diameter 0.45um Gelman Supor-450 membrane filter and 47mm diameter Whatman GF/C glass fibre prefilter)

3. One 60ml syringe (Charise)

4. Four 150ml polyethylene sample bottles

5. Two 100ml polyethylene sample bottles

B. COLLECTION

1. Rinse four sample bottles three times each with DI water.

2. Fill one 100ml bottle with approximately 50ml of DI water. Label "DI Blank #1". Analyze for O-PO_4.

3. Fill one 150ml bottle with approximately 100ml of DI water. Label "DI Blank #2". Preserve with H_2SO_4. Analyze for NH_3 and $NO_2 + NO_3$.

4. Fill one 150ml bottle with approximately 100ml of DI water. Label "DI Blank #3". Preserve with HNO_3. Analyze for trace metals.

C. FILTRATION

See Dissolved Nutrients or Metals, Section 11.9.2, for collection methodology, and for filtration procedure. Fill the second 100ml bottle with 50ml of filtrate. Label "Filter Blank #1." Analyze for O-PO_4. Fill second 150ml bottle with 100ml of filtrate. Label "Filter Blank #2". Preserve with H_2SO_4. Analyze for NH_3 and $NO_2 + NO_3$. Fill the third 150ml bottle with 100ml of filtrate preserve with HNO_3. Analyze for trace metals.

D. PRESERVATION

Dilute H_2SO_4 for N(provided by laboratory in marked ampules) to compensate for small sample size. No preservative for P.

E. PRECAUTIONS

See Field Collection Procedures, Section 10.4, for special precautions.

F. QUALITY CONTROL

Use only DI water taken from carboy used by Laboratory Analyst to prepare standards. This is the freshest DI water in the laboratory.

G. SPECIAL INSTRUCTIONS

1. Use only apparatus prepared using Equipment Preparation Procedure, Section 11.1.

2. Filter blanks may be prepared in either the laboratory or the field. The primary purpose of the blanks is to check the thoroughness of the procedure for acid-cleaning filtration apparatus and to check for contaminants in the filters.

H. REFERENCES None

I. PROJECT

Clark Fork Basin Study, NPDES Compliance Monitoring, Intensive Surveys

11.11.2 Field Blanks

A. EQUIPMENT

One 250ml polyethylene bottle filled with DI water

B. COLLECTION

Rinse bottle three times with DI water. Fill bottle nearly to top and cap.

C. FILTRATION None

D. PRESERVATION

Transport bottle to field. At the end of the field study, preserve sample with HNO_3 for trace metals and H2SO4 for total nutrients. Return to laboratory for analysis.

E. PRECAUTIONS

1. Make sure bottle has been acid-soaked according to Equipment Preparation Procedure, Section 11.1.

2. Determine whether the preservative ampule shall be a Teflon ampule or a regular laboratory preservative ampule.

F. QUALITY CONTROL

Use only DI water taken from carboy B in the Chemistry Laboratory. This carboy is used most frequently and water in it is therefore replaced often. It is also the water used in the preparation of laboratory standards.

G. SPECIAL INSTRUCTION

One liter bottle may be needed for analysis of certain metals or nutrients.

H. REFERENCES None

I. PROJECT

Clark Fork Basin Study, NPDES Compliance Monitoring, Intensive Surveys.

11.11.3 Duplicates

A. EQUIPMENT

1. Sample bottles (1L or 25ml polyethylene bottles)

2. Preservatives

B. COLLECTION

1. Samples are collected following Water Collection Procedures, Section 11.9.1, (Grab Samples) and procedures for the particular parameters of interest (i.e., TSS, Dissolved Nutrients, etc.).

2. When collecting duplicate samples, all steps performed in collecting one sample (or set of samples) shall be repeated so that two samples (or sets of samples) have been collected.

3. Ideally, duplicates shall be submitted to the laboratory under a fictitious name that is recorded in the field notes or log book. Due to the laboratory's familiarity with the DEQ's long term sampling programs, "fictitious" names often arouse suspicion and it is debatable whether such precautions accomplish their objectives. Fictitious names are usually more successful in one-time surveys or short term surveys where laboratory analysts are unfamiliar with sampling locations. Duplicates may be submitted to the laboratory labeled as "Duplicate" samples.

4. Duplicates must be handled identically (temperature, preservation, etc.).

C. FILTRATION

Filtration is conducted as required in the procedure appropriate to the parameter(s) of interest.

D. PRESERVATION

Samples are preserved as necessary to meet EPA requirements. It is important that duplicates be handled (temperature, preservation, etc.) identically.

E. PRECAUTIONS

1. It is important that duplicates are collected under the same conditions. In grab sampling streams, wastewater discharges, etc., this can best be done by collecting them side-by-side and simultaneously, if

possible. Samples collected at different times or at different points in a stream shall not be measuring the error in the collection or analytical process, but the natural spatial or temporal variation in water quality.

F. QUALITY CONTROL

1. Acceptable limits for duplicate sample analyses is defined as a difference no greater than two standard deviations specified in the laboratory's Quality Assurance limits for the appropriate parameter, concentration range, and measurement method.

2. In case duplicate analyses are unacceptable ("Out of limits"):

a) Audit the records (field notes or log book, laboratory records, bench logs, strip charts, internal quality control checks) and evaluate methodology and techniques.
b) Initiate corrective action based on the findings of step a.
c) Submit another duplicate as soon as possible for the constituents in question.
d) Re-evaluate procedures and/or records associated with the new duplicate as soon as possible.
e) Determine the acceptability of data; unacceptable data shall be withheld from the data base; withdrawn from the data base if already entered; or used with discretion.

3. If a duplicate is submitted using a fictitious name, be sure appropriate steps are taken to prevent its being entered permanently into the computer or office file as a real sample.

G. SPECIAL INSTRUCTIONS

There is often a temptation to take duplicate samples from a "common bucket" to eliminate temporal and/or spatial water quality variability. While this increases the homogeneity of the sample, it also represents a deviation from the usual sample collection procedure and introduces another possible source of sample contamination. Such a procedure shall be avoided.

H. REFERENCES None

I. PROJECT

Clark Fork Basin Study, NPDES Compliance Monitoring,

Intensive Surveys, Drinking Water

11.11.4 Spikes

A. EQUIPMENT

1. One new four-liter polyethylene cubitainer

2. One clean (preferably acid rinsed) 1000ml volumetric flask

3. One 10ml volumetric pipette

B. REAGENTS

1. Environmental sample

2. Preservatives

3. EPA Quality Control samples

C. PREPARATION

1. Spikes are prepared by diluting a small volume of an analyte of known concentration with an environmental sample (matrix). After analyzing the spike and the environmental sample, the accuracy of the measurement method can be determined by calculating how much of the analyte was recovered.

2. Spikes shall be prepared so that the addition of an analyte increases the sample concentration by 50 to 200 percent. This requires that the environmental sample collected have measurable concentrations of the constituents of interest, preferably at a minimum concentration of 5X the detection limit. Historical data shall be reviewed to determine possible sources of environmental samples. Slightly to moderately polluted waters (i.e., below wastewater treatment discharges, streams affected by acid mine drainage) are good prospects.

3. Select an EPA Quality Control sample to use for the spike. Select one that, based on the review of historical data, shall increase concentrations of the constituents of interest 50 to 200 percent.

4. Collect the environmental sample in the four-liter cubitainer. Rinse three times before filling, and preserve with an adequate amount of the appropriate preservative. Handle and ship as any other sample.

5. Consult instructions for EPA Quality Control samples for specific preparation instructions. Generally, 10ml of the QC sample are pipetted into the volumetric flask, then diluted to 1000ml with the environmental sample (procedure may vary depending on the constituent of interest). Mix thoroughly.

6. Transfer the spiked sample to a regular sample bottle. The spike is identified and is recorded in the field notes or log book.

7. Transfer the environmental sample to a regular sample bottle and label with the proper identifying information.

8. The sample and spike must be handled identically (temperature, preservation, etc.), and analyzed for the same parameters.

9. Submit both spike and sample to the laboratory in a routine manner.

D. PRECAUTIONS None

E. SPECIAL INSTRUCTIONS

1. Acceptable spiked sample analyses are recoveries within the acceptance limits specified in the Chemistry Laboratory's Quality Assurance Limits for the constituent, concentration range, and analytical method of interest. Percent recovery is calculated as

$$100 \times (A-B)/D$$

Where A = concentrations of matrix & spike
B = concentration of matrix
D = actual spike concentration

2. In case analyses are unacceptable ("out of limits"):

a) Audit the records (field notes or log book, laboratory records, bench logs, strip charts, internal quality control checks) and evaluate methodology and techniques.
b) Initiate corrective action based on the findings of step a).
c) Submit another duplicate as soon as possible for the constituents in question.
d) Re-evaluate pro cedures and/or records associated with the new duplicate as soon as possible.
e) Determine the acceptability of the data. Unacceptable data shall be withheld from the data base, withdrawn from the data base if already entered, or used with discretion.

3. If a spike is submitted using a fictitious name, be sure appropriate steps are taken to prevent its being entered permanently into the computer or office files as a real sample.

F. REFERENCES None

11.11.5 Reference Sample

A. EQUIPMENT

1. One clean (preferably acid rinsed) 1000ml volumetric flask

2. One 10ml volumetric pipette

B. REAGENTS

1. One reference sample

2. Preservatives

3. Deionized water

C. PREPARATION

Reference samples are prepared by diluting a small volume (10ml) of an analyte of known concentration to 1 liter with deionized water and adding the required preservative. The reference sample has a known confidence interval that must be achieved by a USEPA certified laboratory and shall be run with all samples for QA/QC.

D. PRECAUTIONS None

E. SPECIAL INSTRUCTIONS

Reference samples are run by the Chemistry Bureau routinely. Documentation of reference sample QA/QC is available from the Chemistry Bureau on demand.

F. REFERENCES None